

APPLICATION

FOR

UNITED STATES LETTERS PATENT

TITLE: **QUANTUM EFFICIENT PHOTOACID GENERATORS
FOR PHOTOLITHOGRAPHIC PROCESSES**

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Express Mail No. EV 337 932 476 US

Date: September 17, 2003

**QUANTUM EFFICIENT PHOTOACID GENERATORS
FOR PHOTOLITHOGRAPHIC PROCESSES**

Background

This invention relates to making semiconductors and,
5 particularly, to photolithography.

In photolithographic processes, a photoresist is deposited. The photoresist is exposed to radiation via a mask. Some regions of the photoresist develop away and other regions remain.

10 In order for the photoresist to be most effective, especially in connection with advanced lithographic processes, it should be highly transparent. For example, in connection with 157 nanometer and extreme ultraviolet lithography, the photoresist may absorb too much of the
15 incident radiation. While those photoresists were fully effective for prior generations of lithographic technology, with more modern lithographic techniques, these photoresists may be deficient with respect to their transparency. In particular, the existing photoresists may
20 be too radiation absorptive, which degrades the patterning performance of the resist.

Conventionally, the photoresists have photoacid generators which, upon exposure to radiation, generate acids that implement the breakdown of the photoresist where
25 exposed. Current photoacid generators are not optimized

for changes in polymer resins that are implemented to improve transparency. As a result, phase separation may occur due to structural differences.

Thus, there is a need for alternate, transparent
5 photoresists.

Brief Description of the Drawings

Figure 1 is a depiction of a cation in accordance with one embodiment of the present invention;

Figure 2 is a depiction of a cation in accordance with
10 one embodiment of the present invention; and

Figure 3 is a depiction of a cation in accordance with one embodiment of the present invention.

Detailed Description

Photoacid generator compounds may exhibit improved
15 transparency in comparison to materials currently being used in 157 nanometer and other lithographic technologies. These compounds may maintain sufficient quantum yield under irradiation for chemically amplified photoresists. The photoacid generators may also have improved compatibility
20 with the resin matrix making up a photoresist, in some embodiments.

The photoacid generators may include anions and cations. The cations may have single or sigma bonds using orbital overlap, rather than conventional pi or double
25 bonded species. These sigma-bonded species may enable

absorbent moieties to trigger photochemical reaction mechanisms that produce acid upon irradiation of the catalyst precursor by vacuum ultraviolet and ionized radiation, such as, for example, electron beam, ion beam, 5 and extreme ultraviolet lithography processes. The absorbent sigma-bonded moieties may be linked to catalyst precursors as triggers for catalyst formation. Absorption of 157 nanometer electromagnetic radiation, triggering catalyst formation, from a catalyst precursor with sigma- 10 bonded moieties, may be less than with conventional technologies.

The use of absorbing moieties that have reduced absorption at longer wavelengths enable photogenerated catalyst design that may be optimized to 157 nanometer 15 lithography with chemically amplified photoresist in some embodiments. Moieties of the form C-R and C-X, where R may be a hydrogen, an alkyl, a substituted alkyl, and X may be a halogen, a chalcogen or other heteroatoms may be used as catalyst precursors for chemically amplified photoresist 20 for 157 nanometer radiation may be applied. While the fundamental deprotection mechanism common to chemically amplified photoresists may remain unchanged in some embodiments, the classical mechanism may occur without a decrease in overall resist transparency that is typically 25 encountered by the present state of the art photoacid generators.

Currently, many of those skilled in the art have focused primarily on developing polymer resins with very low transparencies in order to facilitate resist patterning for 157 nanometer technologies. While this focus on
5 developing low transparency resin has been a key enabler of the technology thus far, those skilled in the art are still primarily using photoacid generator materials optimized for longer wavelengths developed in earlier technologies, such as phenyl-based materials.

10 While phenyl-based materials do have good quantum efficiencies, these materials are highly absorbing at 157 nanometer and thus, are not fully optimized for applications at 157 nanometers. The sigma-bonded species are both highly transparent and have sufficient quantum
15 yields at wavelengths of interest to further reduce the overall absorbance of the resist, thereby improving patterning performance. Additionally, due to structural similarities, the sigma-bonded photoacid generators also may be more compatible with polymer resin than conventional
20 classes of photoacid generators.

In particular, the cation portion of the photoacid generator, which is the photon harvesting part, may be modified so that it is sigma-bonded. The highly conjugated phenyl groups typically involved in conventional techniques
25 are replaced by moieties primarily comprising C-H and C-F single bonds. The reduced conjugation reduces the

absorption, especially at 157 nanometers, and thereby improves the overall performance of the resist due to lower absorption. At the same time, photoacid generators that are sigma-bonded still exhibit sufficient quantum
5 efficiency to be viable in photoresists through absorption of radiation coupled to bond scission.

Photoacid generators perform two coupled processes. First, radiation is absorbed by a competent moiety whose orbital energy is mated to photons. For longer wavelengths
10 this has been accomplished through the application of pi-bonded species in conjugation. Such antenna moieties are efficient absorbers at longer wavelengths.

In the second process, photoacid generators fragment and form acid after radiation is absorbed. Thus, the
15 energy from the radiation is coupled to bond breaking processes. At longer wavelengths, the efficiency of absorption is relatively low, necessitating multiple absorbing moieties on the photoacid generator. For example, triphenylsulfonium nonaflate has three radiation
20 absorbing phenyl groups. The energy for bond breaking reactions is facilitated from efficient collection of radiation.

At shorter ultraviolet wavelengths of 248 to 193 to 157 nanometers, the efficiency of radiation absorption by
25 molecular species improves, because the radiation is more energetic and capable of exciting more different kinds of

chemical bonds. Indeed, few bonds do not absorb at 157 nanometers, complicating resist design.

At 157 nanometers, photoacid generator efficiency is not limited by absorbance, as the photoacid generator molecules are highly absorbing. The high absorption, while not materially improving quantum efficiency, does increase absorption significantly.

The conjugated moieties, such as phenyl groups, may be reduced or eliminated from the cation with the concomitant introduction of more transparent sigma-bonded moieties, such as substituted alkyl groups. The use of sigma-bonded moieties results in photoacid generators that still absorb in proximity to the site of bond scission, allowing coupling of absorption and fragmentation.

As an example, instead of using a conventional cation, the addition of a methyl iodide to a stirred solution of diisopropylsulfide in toluene, heated below reflux, may result in sigma-bond formation. Crystalline diisopropylmethylsulfonium iodide is isolated by evaporation and purified by recrystallization. Photoacid generator formation is accomplished by an ion exchange from the silver nonaflate. Ion exchange to make nonaflate sulfonium salt from sulfonium halide may result in the formation of a sulfonium halide and may follow procedures known in the art.

Referring to Figure 1, an exemplary cation is illustrated that uses a base atom, such as a sulfur atom, coupled to three moieties indicated as R', R'', and R'''. In this embodiment, each moiety R is coupled by a single bond to the base atom. The moieties R may comprise an alkyl or substituted alkyl (halogen, ethers, esters, carbonates, ketones, or other functionally consistent moieties) to mention two examples. In the embodiment illustrated in Figure 1, all of the moieties coupled to the base atom are single bonded and, in some embodiments, all of the bonds within each of the moieties R may be single bonded.

Referring to Figure 2, the base atom, such as a sulfur atom, may be coupled to the moieties R' and R'', as in Figure 1. In this case, the moiety R''' is replaced by a chain of length n coupled through a double bond to a moiety X, in turn coupled to moieties R₁ and R₂. The chain may also be coupled to a moiety R₃. Each of the moieties R₁, R₂, and R₃ may be any of the alkyl or substituted alkyl, for example. Morphology may be rings, chains, or branched structures, to mention a few examples. The element X may be carbon, nitrogen, sulfur, or phosphorus. The chain, indicated as n, may be any length. Thus, in this example, the number of double bonds may be reduced, but some double bonds may still be present. The number of double bonds is reduced to improve transparency compared to that of phenyl-based, conventional cations.

Referring to Figure 3, in this case, the base atom (i.e., sulfur) is coupled to the moieties R' and R'' as before. The base atom is also coupled through a chain of length n to a moiety R_1 , in turn coupled to a double bond, 5 coupled to X . The double bond may also be coupled to the moiety R_2 . In this case, the moieties R_1 and R_2 may include oxygen and some other elements. X , R_1 , and R_2 may be carbon, nitrogen, sulfur, or phosphorus. The chain n may be of any length. Again, the number of double bonds 10 coupled to the base atom are reduced, but some double bonding is still permitted. Advantageously, the double bonding is reduced sufficiently to improve transparency over that of conventional phenyl-based cations.

While the use of single bonded systems, rather than 15 double bonded or aryl systems is suggested in accordance with one embodiment of the present invention to ensure adequate quantum efficiency while decreasing the overall absorbance, it is also anticipated that modification of the anion portion of the photoacid generator may also be 20 implemented. For example, the use of a more weakly coordinating, non-basic ion to form a stronger conjugate Bronsted acid is one example of a modified anion portion. In another example, the loading or concentration of the photoacid generator may be modified in the photoresist 25 system to further improve quantum yields versus aryl systems. The anion modification and the concentration

modification would not detrimentally affect resist performance from issues such as defects or solubility.

Additionally, while the focus of one embodiment of the present invention is not specifically on the anion portion
5 of the photoacid generator, the new classic cations described herein is considered compatible, not only with perfluoroalkyl sulfonate (PFAS) or perfluorooctyl sulfonate (PFOS) anions, but also with new, more novel anions which are considered more environmentally friendly, such as imide
10 and methide systems recently disclosed. See Lamanna et al., "New Ionic Photo-Acid Generators (PAGs) Incorporating Novel Purfluorinated Anions," Proceedings of SPIE Vol. 4690 (2002).

While the present invention has been described with
15 respect to a limited number of embodiments, those skilled in the art will appreciate numerous modifications and variations therefrom. It is intended that the appended claims cover all such modifications and variations as fall within the true spirit and scope of this present invention.

20 What is claimed is: